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X-Ray Fluorescence Analysis at the Naval Research Laboratory

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<p>This essay outlines the significant work of one group at the Naval Research Laboratory (NRL) during 50 years of leadership in X-ray Fluorescence Analysis (XRF). NRL has produced many of the developments that make XRF analysis the quantitative method that it is today, including the first XRF spectrometer with electronic detection, multichannel analysis of energy dispersive XRF detectors, and public domain software for quantitative analysis. The NRLXRF computer program incorporated fundamental parameters as well as the empirical coefficient methods and treatment of particle size effects into one cohesive and flexible package. The fruits of this research, including the NRLXRF computer code, were actively transferred to industry where they ripened into products which became important in mining, manufacturing, and metals recycling. This legacy continues with the development of technologies for environmental cleanup and for wear monitoring of high value machinery.</p>			
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X-RAY FLUORESCENCE ANALYSIS
AT THE NAVAL RESEARCH LABORATORY
1948 TO 1997

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INTRODUCTION

In the 50 years that the Naval Research Laboratory has been involved in X-ray Fluorescence Analysis, there have been many developments which have made the technique what it is today. Many of the advances owe at least part of their success to the contributions made by the scientists of a specific group. This essay will present one man's opinion of the significant work by members of that group, as related to the impact that X-ray Fluorescence Analysis has had on the field of analytical chemistry in general.

It must be pointed out that the development of X-ray Fluorescence Analysis (XRF) at the Naval Research Laboratory (NRL) was carried out primarily by one group of workers. That group was known by several names over the years, beginning as the Electron Optics Branch, evolving into the X-ray Optics Branch for most of the time period, called the Condensed Matter Physics Branch for some time, and, as this is written, the Dynamics of Solids Branch.

HOW IT BEGAN

The Early Years

In order to appreciate the work which was carried on in X-ray Fluorescence Analysis at the Naval Research Laboratory, it is necessary to recount some of the work which preceded it. Although the impetus for x-ray fluorescence analysis was inspired by Moseley's landmark work in 1913¹, that was preceded by several developments important to Moseley's efforts. Obviously, the occasion of the discovery in 1895 by Röntgen of the penetrating nature of the radiation emitted from a cathode-ray tube², which he named x-rays because of its unknown nature, was the necessary beginning. Well after the utility of imaging through opaque objects had been demonstrated, Barkla, et al, observed in 1908³ that, when elements were irradiated with primary X-rays, the secondary emitted radiation varied in penetration power (as measured by absorbing the rays with foils). Barkla demonstrated that the total attenuation of the incident X-ray beam was different depending on whether the absorber was placed either between the source and the scatterer, or between the scatterer and detector. From this observation Barkla concluded that the scatterer was not only scattering - but it was also modifying the beam. He further concluded that *hard* primary radiation could produce *soft* secondary radiation. It was Barkla who coined the term "characteristic rays"; he also observed that there were two components to this radiation, a "harder" and a "softer" one (specified by its ability to penetrate the foils), choosing to name them as K and L rays,

respectively, starting in the middle of the alphabet, assuming yet "harder" and "softer" radiation would be discovered.

Over the next two-and-a-half decades, many workers investigated the development of the field, including the applications of interest. Beatty⁴ demonstrated that the characteristic rays could be generated directly by interaction with electrons; Friedrich and Knipping, working with von Laue showed⁵ how crystals diffract characteristic x-rays; the Braggs built a crystal spectrometer and measured the spectrum from a platinum target; and de Broglie described⁷ how specimens outside the x-ray tube could be excited to emit their characteristic photons by fluorescence. In his treatise on the x-ray spectra¹, Moseley had proposed that the relationship between wavelength and atomic number might lead to the discovery of elements missing from the Periodic Table. In 1923, this was achieved by Coster and von Hevesy⁸ when they identified Z = 72 (hafnium) by its characteristic x-ray spectrum emitted by a zircon from Norway. One more significant development occurred during this period: Jönsson⁹ adapted the newly-developed Geiger counter to measure primary x-ray spectra. It is possible to judge the applicability of XRF during this time by recognizing that Eddy and Laby¹⁰ were performing x-ray spectrochemical analysis of trace concentrations in 1929. The period from 1932 to 1947 can best be described as the "lost years" with respect to XRF. During this period, not one reference to chemical analysis by x-rays can be found in *Chemical Abstracts*, in spite of the work which had gone on before.

THE "FORMATIVE YEARS"

NRL enters the picture

While the impact of research at the Naval Research Laboratory was necessarily an evolutionary process, this report will deviate from a strictly chronological listing of developments at certain places, in order to make a coherent exposition. It is also necessary to reference developments from other institutions, in order to present the NRL work in context. A chronological listing of some NRL contributions is given in Table 1. In addition, while this document is primarily concerned with XRF, there were certain developments from research efforts in the field of Electron Probe Microanalysis (EPMA) that had a direct impact on XRF.

The period from 1947 to the middle 1960's can be characterized by tremendous advances in the practice of XRF. That is not to say that the most recent 30 years have been devoid of developments, but as the field has matured, progress becomes slower and less frequent. Perhaps the first example of an effort at NRL that had some relevance to XRF is reflected in a paper published in 1942¹¹, in which Friedman, et al., described the application of the Geiger-Müller counters to replace photographic film or fluorescent screens in radiographic examination of opaque objects. This was the work which ultimately led to the first x-ray spectrometer; in 1947, Friedman and Birks, cooperating as members of the X-Ray

Table 1. SIGNIFICANT CONTRIBUTIONS TO XRF BY NRL
 * Believed to be a first

AUTHORS	CONTRIBUTION	DATE/REF.
Friedman & Birks	*Geiger Counter for XRF	1948/Ref. 12
Birks	*Vacuum X-ray Spectrometer	1951/Ref. 16
Birks, Brooks & Seal	Medical Application of XRF	1951/Ref. 14b
Birks & Brooks	*Uniform Bending of Crystals	1953/Ref. 26
Birks & Brooks	Application of Curved Crystals	1955/Ref. 25
Birks & Seal	*Properties of LiF	1957/Ref. 24a
Birks & Siomkajlo	Long-Spacing Crystals	1962/Ref. 23
Birks & Batt	*Use of Multichannel Analyzer	1963/Ref. 21
Birks, Seibold, Batt & Grosso	*Comparison of Protons, Electrons and X-rays for Excit.	1964/Ref. 19
Birks, Labrie & Criss	*ED for Quantitative XRF	1966/Ref. 20
Gilfrich & Birks	X-ray Tube Spectra	1968-75/Ref. 90-93
Criss & Birks	Fundamental Parameters	1968/Ref. 84
Birks, Gilfrich & Burkhalter	Pollutant Analysis by XRF	1972-75/Ref. 29-37
Gilfrich, Brown & Burkhalter	*Efficiency of Crystals	1975/Ref. 24c
Criss	Particle Size - Pollution	1976/Ref. 87
Birks, Gilfrich & Criss	NRLXRF - Public Domain	1978/Ref. 86
Nagel Barbee Gilfrich et al	Multilayers	1981-92/Ref. 41-58
Gilfrich, Skelton, Nagel, Webb, Qadri & Kirkland	Synchrotron Radiation XRF	1983-92/Ref. 61-68
Dozier, Freitag, Gilfrich, Kirkland, Newman, et al	Capillary Optics	1994-96/Ref. 69-71

Optics Branch of NRL, were studying steel samples by powder x-ray diffraction. As was usual with this technique, they were using a copper x-ray tube and they noticed the fog (high background) on the film. They interpreted that problem as fluorescence of the iron excited very efficiently by the copper radiation, and remembered that this phenomenon had been used as an analytical technique years before. It was at that time that an instrument was assembled using available components to first employ what has become the basic geometry for Wavelength Dispersive XRF (WDXRF) spectrometers, even for modern analyzers. Converting an x-ray diffractometer, and combining the advantages of de Broglie's fluorescent excitation with Jönsson's Geiger counter detector, the instrument used an end-grounded, high intensity, thin window sealed tungsten-target x-ray tube, either (200) NaCl or (220) CaF₂ analyzer crystals, a Geiger counter with a special thin mica window, a collimator laboriously constructed of thin-walled nickel tubing, and a turret device to facilitate changing specimens¹². In the next few years, the NRL scientists applied this instrument to several types of analytical problems: the systems hafnium-zirconium and tantalum-columbium were studied¹³; the determination of tetra-ethyl lead in aviation gasoline^{14a} and hemoglobin in blood^{14b}; and the analysis of uranium solutions¹⁵.

The NRL instrument, as it existed during this time, had several limitations. The Geiger counter could only tolerate a limited count rate without becoming saturated; only those wavelengths which could be measured in an air atmosphere were accessible; and the crystals available were less than optimum, the most efficient (NaCl) being subject to deterioration in a humid atmosphere. Over the next few years, these limitations were overcome, with much instrumental and analytical progress resulting from work at NRL. The limitation to those wavelengths which could be measured in an air atmosphere would be overcome by introducing helium into the path of the x-rays, or evacuating that path. Helium presents some inconvenience due to the problem of maintaining a stable atmosphere. An instrument providing a vacuum environment for measuring longer wavelength x-rays was developed at NRL¹⁶. It was several years, however, before a commercial vacuum spectrometer became available. The difficulty with the limit on the Geiger counter count-rate was conquered by the development of the scintillation and gas-proportional counters, largely by the nuclear physics community¹⁷. Although the development of these detectors was not an NRL contribution, some of the applications took advantage of the higher count-rate tolerance. More importantly, the ability to discriminate the photon energy of the radiation being detected set the tone for the stature achieved by NRL in the field.

One of the important parameters in determining the intensity of an element excited by primary photons is the excitation efficiency. L.S. Birks studied this parameter for K-series x-rays of 14 elements from Ti (22) to Ag (47), and for primary wavelengths from 0.3 Å to the K-absorption edge of each element, using a proportional counter to measure the intensity of both the primary and the excited (fluorescent) radiation¹⁸. In this case, the primary radiation was selected by crystal monochromatizing a portion of the continuum from an x-ray tube, or by exciting the secondary radiation from a fluorescer. Because the proportional counters were energy sensitive, the radiation of interest could be isolated from any spurious radiation, which otherwise would have introduced errors. Working with other members of the NRL group, Birks then compared the excitation of characteristic x-rays by protons, electrons and primary x-rays, again taking advantage of the energy discrimination ability of the proportional counter¹⁹. These last two references were important in the development of

two sub-fields in the general area of XRF, Energy Dispersive X-ray Fluorescence (EDXRF) and Particle Induced X-ray Emission (PIXE). The application of EDXRF (using proportional counters) for quantitative analysis was described in an NRL report and later published in the open literature, again by Birks and coworkers at NRL²⁰. The use of an energy sensitive detector to perform XRF measurements requires that an electronic system be available to record the variable-amplitude pulses from the detector; initially, a single channel pulse amplitude discriminator was scanned through the appropriate range to record the signals. When the Multichannel Analyzer (MCA) was developed (again by the nuclear physics community), it became obvious that it could have a significant impact on EDXRF. One of the first applications of the MCA to x-ray analysis was at NRL, where the instrument was used to record the intensities generated in EPMA²¹; the Electron Probe Microanalyzer by Birks and Brooks at NRL was one of the first developed in the United States²².

FURTHER DEVELOPMENTS

NRL makes an impact

With the development of the vacuum spectrometer, it became incumbent on the XRF community to develop analyzing crystals with larger interatomic spacings in order to use the crystal spectrometer to disperse the longer wavelengths. While mica and gypsum had been available, they were unsatisfactory for a variety of reasons. Attempts to locate suitable candidates led the NRL group to examine several metal-organic crystals²³. Of all the crystals surveyed, potassium acid phthalate (KAP) was determined to be the best, and it became the workhorse for the wavelengths in the range of 10-25 Å. Over the years, KAP has been replaced for this wavelength range by the rubidium and thallium salts of this organic compound, more efficient because of the higher atomic number cation.

The shorter wavelength region was not being ignored. With the development of synthetic lithium fluoride (LiF)^{24a}, the (200) cleavage plane became the most efficient analyzing crystal for the 0.5 to 3.5 Å range, replacing rock salt (NaCl), which was subject to the atmospheric humidity. The graphite crystal, not really a single crystal but a highly oriented polycrystal, provided very efficient diffraction characteristics for the slightly longer wavelengths. The diffraction efficiency of LiF can be controlled to some extent by the treatment the crystal is given. The NRL scientists conducted a study of means to improve that efficiency, and made a comparison with graphite, which demonstrated that the larger efficiency for graphite was due in large part to its broad rocking curve^{24b}. The absolute diffraction efficiency (the integral reflection coefficient) is a parameter which is needed in a variety of experiments; Gilfrich and NRL coworkers measured several of the most common crystals as a function of wavelength and compared them to one another^{24c}.

With the development of EPMA, a need arose for curved crystals; the point source of x-rays excited by the focussed electron beam could use a curved crystal to advantage to concentrate the emitted intensity at the detector. Also, some versions of multiple-spectrometer instruments used curved crystals with slits instead of collimators to save space. For effective use of such a dispersing device, a special spectrometer was required; application of such an instrument seemed to be obvious, both to microanalysis and simultaneous analysis²⁵. Initially, most of the work was toward elements that could be

measured in an air atmosphere, thus making LiF the obvious choice. Further, being an alkali halide, it could be curved plastically. Birks and Brooks developed a technique for uniform plastic bending which avoided the "peaked-roof" effect²⁶, and which still has utility today.

The development of EDXRF using proportional detectors moved rather slowly, being most useful for small, "table-top" instruments, many using radioisotopes for excitation. In the mid-1960's, the lithium-drifted silicon [Si(Li)] solid state detector, originally developed as a sensor for nuclear radiation, was shown to be useful for the lower-energy x-rays, and the technology has been refined continuously since²⁷. In the same vein, the lithium-drifted germanium [Ge(Li)] and high-purity germanium [HPGe] detectors were developed as more effective devices for the higher-energy x-rays. These types of detectors, with energy resolution better than proportional counters by almost an order of magnitude, have created a situation where EDXRF instruments extant today outnumber all the WDXRF instruments that have ever been used. The application of x-ray analysis to the pollution problem has taken advantage of the adaptability of these solid-state detectors to the variety of analytical approaches: EDXRF using highly sophisticated instruments, PIXE requiring high-energy accelerators, and portable devices for use in the field²⁸.

THE POLLUTION PROBLEM

EPA requirements

To expand on the application of XRF to pollution, the effort at NRL began as a result of contact with a representative of the Environmental Protection Agency (EPA) at the Clean Air Conference in Washington, D.C. in 1970. At the time, very little, if any attention was being expended on evaluation of XRF for the purpose. Over the next decade, much work was done to examine the potential for routine analysis of a variety of pollution specimens, taking advantage of the expertise available at NRL to study the different excitation and detection schemes for particulate air pollution²⁹. NRL also undertook to study the water pollution problem, as well³⁰. Under contract with the EPA, several studies were performed by the NRL group to evaluate applications to specific problems. Initially, the work was intended to examine the general application of XRF to the elemental analysis of particulate material in the atmosphere and in source emissions³¹. The result of that effort led to a decision by the EPA that they should establish an x-ray laboratory at their research laboratory in North Carolina, built around a multiple-crystal simultaneous x-ray analyzer, an instrument produced by four manufacturers. NRL was asked to evaluate the instruments available³². When the selected instrument was installed, NRL participated in the commissioning, and in the evaluation of the initial results.

The use of large, laboratory-style instruments did not satisfy all of the EPA's requirements, and NRL suggested the possibility of a transportable wavelength-dispersive analyzer which could be moved from place-to-place to make measurements in the field, being transported in a van. It was quite straightforward for NRL to assemble the necessary commercial components with a few custom-built items to produce an instrument meeting the requirements³³, and test it on the roof of a coal-fired power plant in Charlotte, North Carolina. When this prototype analyzer was turned over to the EPA, it was accompanied by

an "Operator's Manual"³⁴, written by NRL. The success of such a field instrument led to a desire for an even smaller instrument, which could be moved around easier, specifically designed to measure sulfur in source emissions. Because of the wavelength of sulfur K-emission, the spectrometer was required to be evacuated, and needed the resolution provided by wavelength dispersion to separate the S K α from the lead L-lines. The analyzer, again fabricated from many commercial components by NRL, had a footprint of less than a square meter and weighed about 25 kilograms^{35,36}. The analysis of pollution specimens for elemental sulfur was significant, but there was a further need to study the valence state of the sulfur. Before the small sulfur analyzer was implemented, NRL demonstrated that the valence state of sulfur could be determined by very simple measurements of the S K β radiation^{37,38}.

The previous effort to study the application of x-ray analysis to water pollution³⁰, was reemphasized by contact from a representative of a different part of EPA, located in Athens, Georgia, who was interested in establishing an x-ray facility. The NRL scientists were charged with two tasks. The first was to evaluate commercial EDXRF instruments by using synthetic samples³⁹ specifically for the analysis of particulate material filtered out of water. The second was to determine a reasonable method for collecting the soluble elements into a form which could be x-ray analyzed. This latter task was performed with the assistance of the Chemistry Division at NRL⁴⁰.

LAYERED SYNTHETIC MICROSTRUCTURES A Major Research Effort

Developments in vacuum technology in the early 1970's and 1980's made highly controllable vapor deposition of materials into a practical technique. One of the applications of this technology relevant to the x-ray field was the production of layered materials by alternate deposition of two different materials. By an appropriate choice of materials, usually a wide atomic number contrast, such a layered material will diffract x-rays, acting like one-dimensional crystals, commonly called Layered Synthetic Microstructures (LSM's). The ability to customize the diffraction characteristics made possible the design of a variety of x-ray instruments⁴¹. Because the vapor deposition systems can be (and usually are) computer controlled, the LSM's can have "graded" layer thickness, either longitudinal or in-depth⁴². Samples of tungsten-carbon (W-C), molybdenum-carbon (Mo-C), niobium-carbon (Nb-C) and titanium-carbon (Ti-C) LSM's produced at Stanford University were provided to the NRL XRF group to be studied; the diffraction characteristics demonstrated that they had relatively broad rocking curves and large integrated diffraction efficiency⁴³ and were very well suited as dispersive devices in wavelength-dispersive spectrometers⁴⁴. Over the next decade, NRL workers studied many different LSM's; these were made up of different pairs of materials (not always elements), on different substrates, having different layer spacings, consisting of uniform and graded spacings, and used for different applications⁴⁵⁻⁵⁰. Concurrent with all the experimental work, attempts were being made at NRL to model the diffraction characteristics of these LSM's. One of the parameters affecting the diffraction efficiency is the roughness of the substrate and how it is reflected in the roughness of the individual layers⁵¹. The theoretical efforts shed some light on the mechanism by which the LSM's functioned as x-ray diffractors⁵²⁻⁵⁸. Because the fabrication of LSM's was most successful for individual layers

of at least 10Å ($2d = 40\text{Å}$), and greater, the devices were most useful for relatively low-energy radiation ($\lambda > 10\text{Å}$). Some of the characteristics of the LSM's required the use of a double-crystal spectrometer. Hence, a special soft x-ray experimental facility was built in the NRL XRF laboratory, using a modified Henke tube source in a high-vacuum chamber, isolated from the experimental chamber of more moderate vacuum by a thin window, with the chamber containing a computer controlled double-crystal spectrometer. This facility was also useful for other experimental measurements requiring a vacuum environment and a high intensity, low photon energy source⁵⁹.

SYNCHROTRON RADIATION

Not just for EXAFS

With the advent of laboratories dedicated to the production of synchrotron radiation (SR), the x-ray community was enthusiastic to make use of the unique properties of such a SR facility. Extended x-ray absorption fine structure (EXAFS) spectroscopy received considerable attention, taking advantage of the high intensity and tunability of the radiation to perform measurements which were difficult, or impossible, using conventional x-ray sources. The use of a continuous source of radiation was ideal for a technique known as energy-dispersive x-ray diffraction, particularly valuable for the x-ray studies of materials at high pressure. One of the scientists of the NRL group, on a sabbatical at the Stanford Synchrotron Radiation Laboratory (SSRL) in California, was using a beam line providing continuum radiation to examine materials in a diamond high-pressure cell. He offered some beam time to his NRL colleagues to make preliminary measurements of the application to XRF. Although some previous synchrotron radiation XRF (SRXRF) studies had been used for specific purposes⁶⁰, this was the first general survey of the use of SRXRF to analyze for elements across the periodic table⁶¹. The specimens used to establish thin-sample detection limits in these experiments consisted of commercial thin deposits of elements and simple compounds on mylar substrates, and solutions at different concentrations deposited and dried on filter paper. Very soon after, further measurements were made by the same group at the NRL beam line newly established at the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory on Long Island, New York, using crystal monochromatized monoenergetic x-rays⁶². The NRL beam line at NSLS was built primarily as an EXAFS facility, but has been used for a variety of x-ray experiments, including the XRF as detailed above, powder and single crystal x-ray diffraction (XRD), and detector calibration. These NRL workers demonstrated that elemental analysis could be performed during EXAFS measurements, using a technique called appearance potential x-ray fluorescence (APXRF), in which the height of the absorption edge jump was a measure of the concentration of the absorbing element^{63,64}, making structural and elemental information available from the same measurement. The status of SRXRF at the time was detailed in an invited paper given by Gilfrich at the 1988 Denver X-ray Conference⁶⁵. The practicality of using SRXRF for specialized analysis was shown by the determination of the trace metal concentrations in individual tree rings⁶⁶, using sub-millimeter beam sizes.

The NRL beam line at NSLS made use of what is referred to as "bending-magnet radiation" from the electron storage ring. An insertion device, known as a "wiggler", makes available even higher intensity, higher photon energy x-rays; scientists from the NRL group

have access to such a beam line. It is important to know the characteristics of the x-ray beam available at such a beam line; we made measurements to determine those features for one of the wiggler beam lines at NSLS⁶⁷. The much higher intensity available to a wiggler beam line make feasible the use of very small beams for microanalysis. Experiments by NRL to define the capability of such small beams demonstrated detection limits for areas of the specimen as small as 10 μ m square⁶⁸.

CAPILLARY OPTICS

Focussing X-rays

The problem of focussing x-rays, or of attempting to make a divergent beam into a parallel one, has been attacked historically by crystal diffraction, a relatively low efficiency process. By taking advantage of the property of total reflection on the inside of small diameter tubes, it is possible to perform those functions with considerably higher efficiency. This idea originated at NRL in 1976⁶⁹ and was made practical in Russia in 1990⁷⁰. By shaping a bundle of these small diameter capillaries in a certain way, it is possible to either focus an x-ray beam to a small diameter spot, or make a divergent beam into a parallel beam with small residual divergence. These properties have considerable application in x-ray analysis as reported by members of the NRL group⁷¹. One of the promising applications of these bundles of capillaries, called "x-ray lenses", takes advantage of the possibility of configuring the input to accept a large solid angle of incident radiation, and produce a beam which is parallel, matched in angle to the rocking curve of a diffracting crystal, so that all the radiation can be directed to a detector. This was demonstrated at the NRL beam line at NSLS⁷². The state-of-the-art of the use of multi-capillary and conic optical elements for parallel beam production was defined in a paper presented at the 1995 Denver X-ray Conference by the NRL workers in collaboration with others⁷³.

MORE ENVIRONMENTAL APPLICATIONS

Miniaturized Instruments

With the development of new technology leading to the miniaturization of many components of x-ray analytical instrumentation, the possibility of in-situ analyzers became a reality. Various parts of the Department of Defense had particular problems with their contributions to polluting the environment. Contractors working for the EPA had demonstrated that portable x-ray analyzers could make a significant impact on the effectiveness of surveying polluted sites for toxic elements⁷⁴. The Army had developed a device called a Penetrometer, which drove an instrumented pipe into the earth to measure the conditions of the subsurface. It contained instrumentation to measure certain organic compounds. NRL suggested that an x-ray spectrometer could be made small enough to fit in a pipe with a one and one-quarter inch inside diameter, to map the metals concentration as the pipe was thrust into the earth⁷⁸. A design was proposed by NRL⁷⁵, and a scenario for the application of an x-ray spectrometer in that Army device was developed⁷⁶. A mock-up of such an instrument in the NRL XRF laboratory showed exactly how it could be deployed in the field to measure the contaminants as the penetrometer was employed⁷⁷. A field test conducted by NRL at the U.S. Army Engineering Waterways Experiment Station in

Vicksburg, Mississippi^{78a} demonstrated the capability of the instrument and showed some improvements which would improve its operation. NRL personnel employed^{78b} an improved model at the Joliet Army Ammunition Plant in Wilmington, IL, to provide semi-quantitative x-ray analysis of the lead concentration as a function of depth below the surface of the landscape.

QUANTITATIVE ANALYSIS

The "Raison d'etre"

The impact that XRF has had on the analytical community is largely due to the fact that it can provide very accurate **and** precise results on the elemental constituents of a wide variety of materials. In the beginning, this was a reasonably tedious exercise, because it required very well characterized "type standards", that is "known" concentration materials as much like the "unknowns" as possible, both in physical form and elemental concentration. The reason for this was the fact of the existence of so-called "matrix effects", the varying absorption characteristics of the elements present in the specimen, and the fact that some elements in the specimen could excite other elements by secondary fluorescence. By using identical specimens as standards, these effects canceled each other. This approach was an effective analytical methodology for routine quality control, where the time and expense of setting up an appropriate cadre of standards could be justified. For other situations, it was necessary to investigate other techniques. It was the development of the mathematical treatment which solved simultaneous equations developed from standards (sometimes as simple as binary standards containing only two elements) to generate empirical coefficients accounting for the effects of each element in the specimen on each other element⁷⁹. While this was a great advantage over a suite of many "type standards", it still required a large number of standards, and frequently the coefficients were applicable over a limited concentration range.

It was at the Philadelphia Navy Yard in the mid-1950's where a scientist named Sherman developed a series of equations which used first principles to calculate the intensity of the various fluorescent x-ray lines generated from specimens of specific concentrations⁸⁰. These equations used basic parameters which are fundamental to the physics of x-ray production, including absorption coefficients, fluorescence yields, jump ratios, and the incident spectrum. The method became known as the "Fundamental Parameter" method. Unfortunately, these equations were quite complex and the computing power available at the time made it impractical to implement them. Furthermore, the parameters were not known in a sufficiently quantitative way to perform effective analysis.

It was not long after that time that the field of EPMA put the calculation of primary (electron-excited) x-ray spectra on a firm basis. The necessity for quantitative electron probe analysis required theoretical calculations because of the difficulty to produce standards (other than pure elements or simple compounds) that were well characterized at the micrometer spatial scale necessary for use as comparison standards. Practical, rather than rigorous, methods of calculating the primary x-ray spectra of macroscopic specimens in EPMA were developed for this purpose by Birks at NRL⁸¹⁻⁸³, and others elsewhere. The calculation of the interaction of electrons with a specimen⁸⁴ was different than computing the interaction of

x-ray photons with materials, but with it now possible to calculate the primary x-ray spectrum, it was time to attack the problem of applying the fundamental parameter method to XRF⁸⁵, taking advantage of Sherman's equations and the advances in computing power⁸⁶, and the fact that D.B. Brown had extended his electron transport code⁸⁷ to calculate x-ray tube spectra more rigorously.

After many years of development at NRL, an XRF computer program (NRLXRF) was published in the public domain^{88,89}, which was so versatile that it permitted pure fundamental parameter calculations, strict empirical data reduction, or a combination of the two, as well as prediction of intensities from proposed specimen concentrations, and treatment of the "particle-size effect"⁹⁰. This approach to data reduction suffered from the uncertainties in the values of the parameters required, some of which had been remeasured previously^{91,92} for comparison to the values in the literature. NRLXRF allowed a well-characterized multielement standard, containing all the elements present in the unknown(s) to be used; this standard minimized the effect of the uncertainties. As mentioned above, the spectral distribution of x-ray tubes used for excitation of the specimen was necessary, and largely unavailable. Although the spectra calculated by Brown's electron transport code had promise, it was computer-intensive, and other available models were not sufficiently accurate to fit the requirements of the fundamental parameter method. The most-used tubes of the time were fitted with either a tungsten or chromium target; experimental measurements were made by the NRL group at usual operating conditions⁹³⁻⁹⁵, for those two, and were supplemented by measurements on the rhodium tube when it became available⁹⁶. With the experimental measurements available, it was possible to compare theoretical models which calculated such spectra. Reasonable agreement between the measured and calculated spectra for the tungsten and chromium tubes^{95,96} (including both continuum and characteristic lines) was shown by Brown, et al., and made feasible the calculation of spectra for any target under any operating condition, making it unnecessary to measure all tubes at all conditions. While the measured spectra were included as parameters to be used in NRLXRF⁸⁹, a simplified calculation algorithm, using a modified Kramers Law, which also demonstrated good agreement with the measured tungsten and chromium spectra, was included to enable the use of other tubes.

CONCLUSION

This chronicle is an attempt to document developments in XRF accomplished largely by members of the NRL X-ray group over almost 50 years. In trying to detail that five decades, I have called upon my own recollections and the large body of papers published by the group, as well as discussions with other members of the group. There have been many more publications which have not been cited; the effort was to choose the papers which had the largest impact on the field. Little reference has been made to the myriad of presentations given over those years, many of them invited, reflecting the prestige with which members of the group were held by the community.

It seems appropriate to mention the three decades (1950 - 1980) during which L.S. Birks was the leader of this group of scientists, a period of time during which XRF reached the level of maturity that it now enjoys, and the esteem that he enjoyed during this period.

One testament to that reputation is the fact that he was elected the first president of the Electron Probe Analysis Society of America (EPASA), now known as the Microbeam Analysis Society (MAS), which has further honored him by establishing an award in his name. A second award, The Birks Award in X-ray Spectrometry, is given in alternate years by the Annual Denver Conference on the Application of X-ray Analysis (The Denver X-ray Conference). Those of us who had the privilege of working with him shall be forever grateful for his tutelage. While not germane to the topic of this document, there were many other areas of x-ray science that were exploited under the direction of Mr. Birks, including both powder and single-crystal x-ray diffraction, high-temperature plasma diagnostics, and the measurement of x-ray spectra to study atomic collisions.

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